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FUNDAMENTAL MATHEMATICAL PRINCIPLES FOR ELECTROCHEMICAL ENGINEERING

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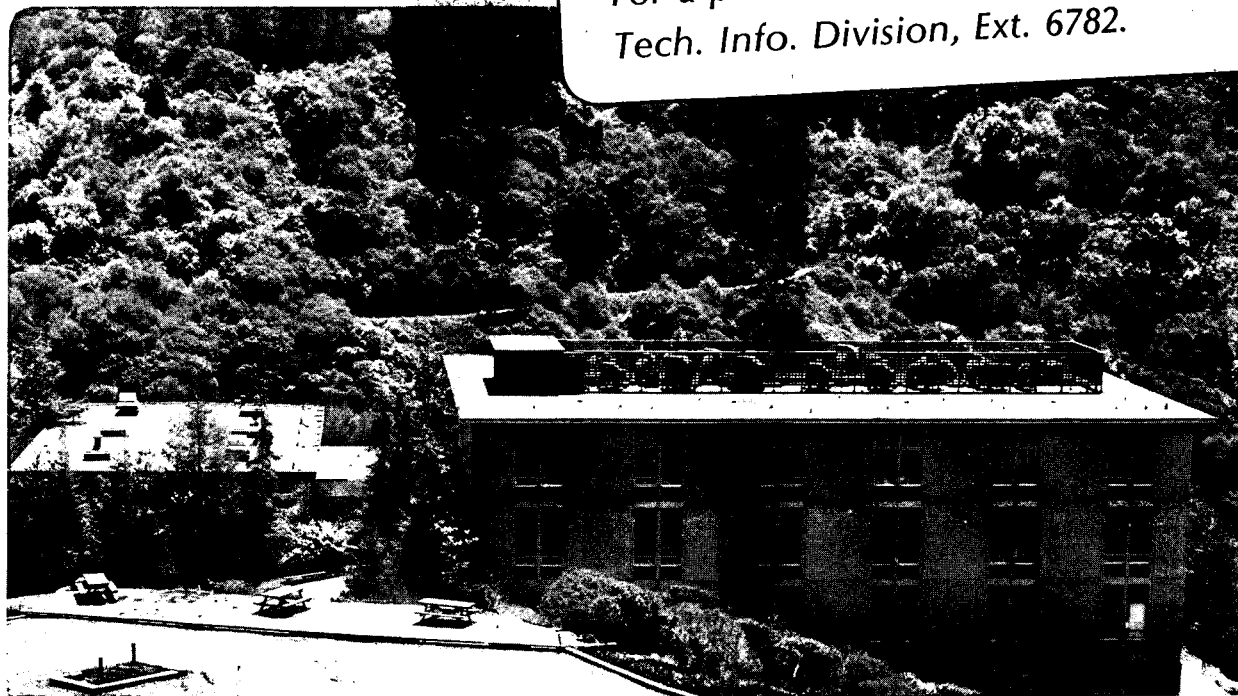
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J. Newman

August 1983

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Fundamental Mathematical Principles  
for Electrochemical Engineering

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August 1983

This work was supported by the United States Department of Energy under Contract Number DE-AC03-76SF00098 through the Assistant Secretary of Conservation and Renewable Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division, and through the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division.

## Introduction

Exceedingly complex processes can now be subjected to reasonably realistic analysis and simulation. Electrochemical processes qualify as complex because of the diverse chemistry involved and the presence of electrical variables. Consequently, we should get on with the job of modeling so that we can simulate electrochemical systems with a completeness and realism comparable to what is found in the simulation of distillation columns.

In this paper we intend to expound on the philosophy of such simulation and to reiterate some of the governing mathematical basis for the physical and chemical processes with which we expect to deal. Examples will be mentioned in order to maintain some flavor of current research problems. These include the use of semiconductor electrodes in a photoelectrochemical cell, the design of LiAl-FeS cells for electrical energy storage, and the growth of a salt film in the corrosion of iron.

## Governing Equations

We intend to model the processes going on inside an electrochemical cell, and for this purpose it is always a good idea to have the governing physical laws firmly in mind. These include laws of transport in electrolytic solutions, a subject reviewed in references 1 and 2.

For many purposes it is sufficient to use dilute-solution theory. There are four equations which we should master here. The material-balance equation can be written

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i . \quad (1)$$

The flux density  $N_i$  contains contributions due to migration, diffusion, and convection:

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + v c_i . \quad (2)$$

The current density in the solution is due to the movement of charged species:

$$i = F \sum_i z_i N_i . \quad (3)$$

Finally, the solution is electrically neutral,

$$\sum_i z_i c_i = 0 . \quad (4)$$

These are the four principal equations that we should remember for electrolytic transport phenomena. For many problems, these need to be augmented by equations of hydrodynamics (a momentum balance and an overall material balance) because the velocity  $v$  appearing in equation 2 still needs to be determined. In other problems, such as porous electrodes, the velocity is determined by the production rates of the various species and the volume changes of the solids, and the momentum balance does not govern.

In all these cases, the governing transport equations need to be augmented by boundary conditions describing Faraday's law and potential losses by electrode kinetics. These are also reviewed in reference 2.

In some applications, the above equations may be modified. The dilute-solution transport relation (equation 2) should probably be replaced by the multicomponent diffusion equation (chapter 12 of reference 2) when dealing with concentrated solutions, ionic melts, or membranes.

### Philosophical Considerations

Approximations are always introduced in the application of governing laws to a real system. Questions then revolve around whether the approximations compromise the validity of the results while helping to make the model tractable mathematically. We can note that in engineering work we are generally interested in scaling up a given system (reference 3). This has the general effect of emphasizing the importance of transport phenomena. A similar dominance of transport phenomena over electrode kinetics occurs for systems operating at elevated temperature.

Historically, the transport-dominated problems have been attacked from one of two extremes (references 2 to 5). In the one extreme, perhaps with an excess of supporting electrolyte, the effect of the migration term in equation 1 becomes negligible, and this term can safely be ignored. If the boundary conditions are appropriately simple, such as a limiting-current condition, then the situation is nearly identical to that prevailing in convective heat transfer and nonelectrolytic mass transfer, and we can use methods and results already developed in those fields. On the other extreme, stirring may be so overwhelming that concentration gradients can be ignored.

Then the cell-design problem reduces to one of solving Laplace's equation, subject to boundary conditions describing the electrode kinetics. This is one of the classical areas in which Laplace's equation was treated mathematically.

As we said at the beginning, electrochemical systems are complex, and we cannot always be satisfied with the approximations represented by the above extremes. To take into account the diverse, interrelated phenomena means that we must take our work seriously. Simplistic analysis is judged to be a useful guide for understanding many features of system behavior, but we need to bring in the computer as a tool for handling everything at once. This does not mean that there is no longer any room for subtlety. A brute-force approach is not being advocated here--although it has its place. Some of the tools presently being used will be illustrated in the examples.

#### Growth of a Salt Film

One of the computer tools now available makes the solution of coupled, nonlinear, differential equations reasonably straightforward (references 2, appendix C, and 6). With this program, BAND(J), we can treat quite complex problems without requiring extensive mathematical approximation. Some problems treated deal with several regions coupled together, for example, the positive porous electrode, the negative porous electrode, and the separator of a battery. Sometimes the thickness of one of the regions needs to be determined as part of the problem. An example is the development of a salt film on a metal undergoing rapid anodic dissolution (reference 7). Figure 1 shows how



we think about the arrangement of the equations and the boundary conditions within the computer for a typical, reasonably complex problem involving coupled, one-dimensional equations--the example being the salt film. Here material balances are written for iron, hydrogen, and total sulfate, and these apply in two regions--the salt film on the left and the electrolytic solution on the right. Boundary conditions are represented by squares. There will be flux conditions at the electrode surface at the far left, and at the junction between the salt film and the solution there will need to be conditions stating that the fluxes are continuous, or are related to the growth of the salt film. These are the square boxes in the middle. An additional statement that the concentrations are continuous is unnecessary because only one concentration variable is used at this internal boundary point (for each species).

Actually four material balance equations could be written, corresponding to the four solute species: sulfate, bisulfate, ferrous, and hydrogen ions. Here it is assumed that the equilibrium between sulfate and bisulfate is rapid. The equilibrium relation replaces the fourth material balance, and the four material balances are added together in such a way as to eliminate the rate of the bisulfate-sulfate reaction. Electroneutrality constitutes the fifth equation; it can be thought of as a governing equation for the potential, even though the potential does not appear in it. The bulk composition and the potential are specified as boundary conditions, represented by the square boxes at the right on figure 1. It is not important whether the four concentrations (and the potential) are specified or only two concentrations are

specified and the remaining two are determined by the electroneutrality and equilibrium conditions. Thus the two right boxes on lines 4 and 5 of figure 1 could be eliminated.

The problem posed here involves the development of the salt film with time. Thus the partial differential equations are stepped through time, and at any time they look to the computer like ordinary differential equations. One realizes that the above description is flawed. The salt-film thickness is not actually known at each time step. Furthermore, the material-balance or flux-continuity conditions at the film-electrolyte interface are too many to fit into the square boxes in lines 1, 2, and 3. To resolve this problem, the salt-film thickness (or actually the change in this quantity over a time step) is added as an unknown variable, one whose value is independent of distance. This strategy leaves us with a box at the film-electrolyte interface, and here we put the remaining boundary condition. Here we have programmed the computer just like the physical problem--the film thickness is unknown and is to be determined by the physical and mathematical processes in the course of the calculation.

The somewhat cruder alternative is to set the salt-film thickness at some arbitrary value, relax the last boundary condition, converge the problem, and compute the error in the unsatisfied boundary condition. Then one must construct a separate loop to determine the value of the salt-film thickness that satisfies the remaining material balance at the interface. This we may do in the course of developing a stable computer program, but the first procedure is more powerful and shows how BAND(J) can be used to program a problem in a manner that parallels the governing laws.

### LiAl-FeS Electrical Storage Battery

Figure 2 illustrates a section through a cell sandwich for a battery. The left portion represents a porous LiAl negative electrode; in the middle there is a porous separator; and the right portion is a porous FeS positive electrode, separated from the separator by a reservoir. The mathematical model is to determine simultaneously the composition, potential, and current density profiles within the LiCl-KCl electrolyte, as well as the discharge curve for the cell potential as a function of time. Figure 3 shows the composition at several times during the discharge.

The one-dimensional model cannot completely represent the resistance of the current collector or grid by means of which current is carried across the face of a plate to a tab or bus. The results obtained above or by means of experiments designed to eliminate the effects of grid resistance can next be embedded into a separate model which calculates the distributions of current density and potential across the face of the plates typical of a battery. By accounting for the weight of the components of the complete cell, one can determine the specific power and specific energy which can be achieved with various designs (see reference 8).

### Photoelectrochemical Cells

Solar energy can presently be converted into electrical energy by means of solid-state, semiconductor devices, and these find application in remote situations despite the high cost. Progress has been made in developing electrochemical cells for the same purpose but

with the use of polycrystalline semiconductor material. This promises to bring down the cost, but it creates some severe corrosion problems which may not have solutions compatible with the energy-conversion requirements. Furthermore, there are questions of scaleup related to the placement of the counterelectrode in relation to the working electrode and incident solar radiation.

We have developed a model for photoelectrochemical cells (reference 9). First, we treated a one-dimensional semiconductor material in which photons were absorbed, a process accompanied by the generation of holes and electrons. Electrons are adsorbed at the interface with different energetics from the bulk, and this created a diffuse charge layer within the bulk of the semiconductor. The same thing occurs in electrolytic solutions at the interface with an electrode, but the thickness of the region of departure from electroneutrality (the Debye length) is much greater in the case of the semiconductor. This is because the concentrations of holes and electrons within the semiconductor are much less than those in dilute aqueous solutions. Furthermore, the dielectric constant is less than for water. Consequently, while for aqueous solutions the region of departure from electro-neutrality can be regarded as part of the interface, for the semiconductor this is the bulk region. Equation 4 must be replaced as a governing equation by Poisson's equation:

$$\sum_i z_i c_i = - \frac{\epsilon}{F} \nabla^2 \phi \quad (5)$$

The model now deals with three coupled differential equations--Poisson's equation and material balances for the holes and the electrons--whose

solution should yield profiles for the electric potential and the concentrations of holes and electrons. The production terms  $R_i$  contain terms due to thermal, as well as photo, generation of holes and electrons and due to recombination. The resulting equations are coupled because the potential and the hole and electron concentrations appear in all three governing equations. The equations are also non-linear, and it is ideally suited for solution with the BAND subroutine. It is also desired to account for complex charge transfer reactions at the interface, charge and mass transfer limitations within an electrolytic solution, and the behavior of the counterelectrode.

After developing the one-dimensional model outlined by these remarks, we may wish to assess the penalty imposed by various cell designs which permit different configurations of the semiconducting electrode relative to the source of illumination and the counterelectrode. We wish to illustrate here the incorporation of the primary resistance of one of these geometries into the model. We do this instead of an exact treatment, which might involve the incorporation of the one-dimensional model of the semiconductor electrode as a boundary condition for a solution of Laplace's equation. For the geometry chosen here (see figure 4), a Schwarz-Christoffel transformation yields the primary current distribution and cell resistance. The use of the computer for the evaluation of the integrals involved yields a practical design tool which frees the investigator from tedious treatment of elliptic integrals. This method, based on the Schwarz-Christoffel transformation, gives accurate solutions to Laplace's

equation with greater computational efficiency than treatment with a relatively coarse finite-difference grid in two dimensions, with an infinite current density at the edge of one of the electrodes.

### Summary

In summary, we should like to reiterate that system simulation and mathematical modeling are aids in cell design and also help fill the gaps in our knowledge and understanding of the chemistry and physics of the processes involved.

### Acknowledgment

This work was supported by the United States Department of Energy under Contract Number DE-AC03-76SF00098 through the Assistant Secretary of Conservation and Renewable Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division, and through the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division.

### Nomenclature

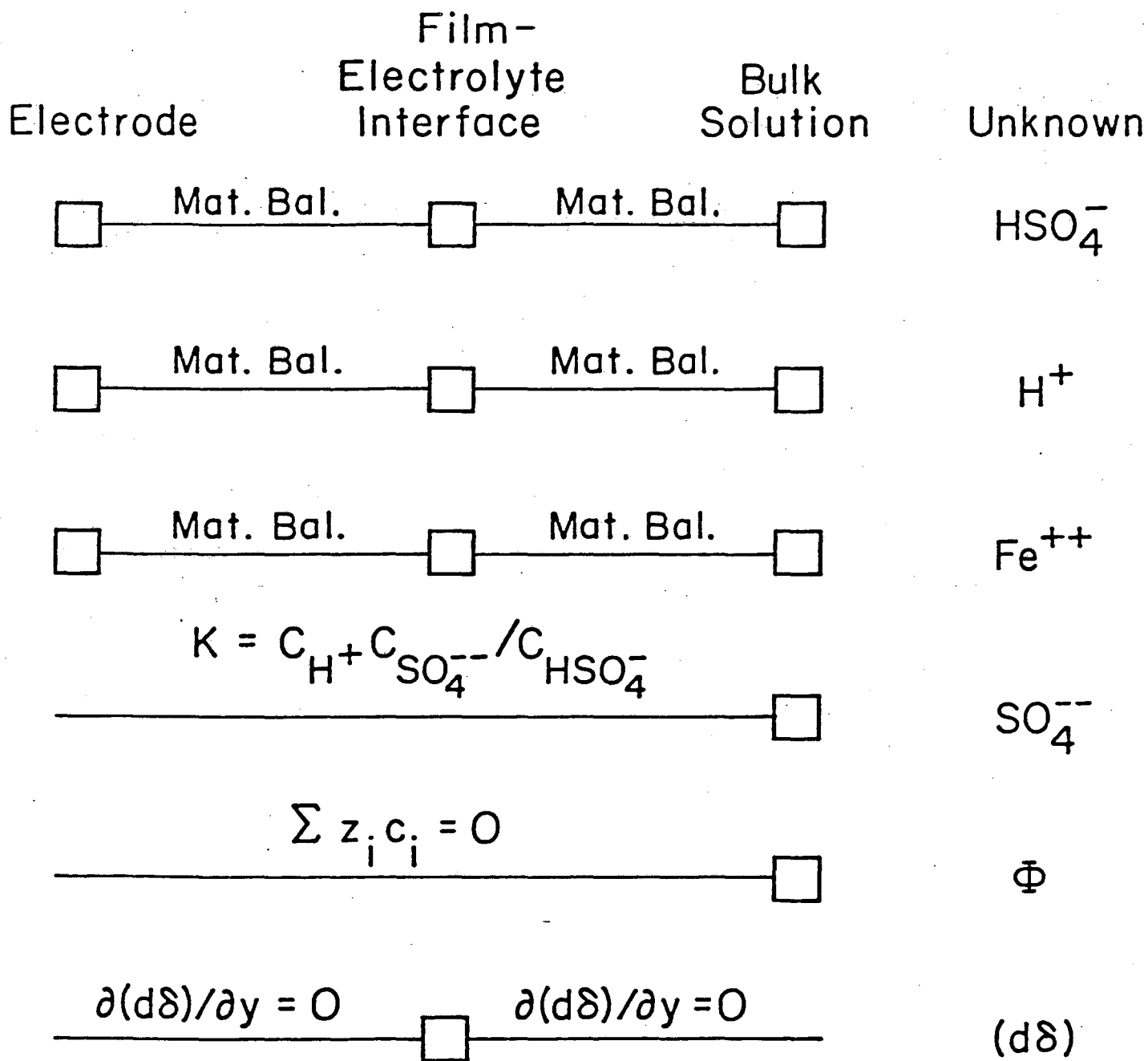
$c_i$	concentration of species $i$ , mol/cm <sup>3</sup>
$D_i$	diffusion coefficient, cm <sup>2</sup> /s
$\epsilon$	permittivity, F/cm
$F$	Faraday's constant, 96,487 C/equiv
$i$	current density, A/cm <sup>2</sup>
$N_i$	flux of species $i$ , mol/cm <sup>2</sup> - s
$\phi$	electrical potential, V
$R_i$	rate of homogeneous production of species $i$ , mol/cm <sup>3</sup> - s

t	time, s
$u_i$	mobility of species i, $\text{cm}^2\text{-mol/J-s}$
v	fluid velocity, cm/s
$z_i$	charge number of species i

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# Structure of Equations



□ Boundary Condition

— Governing Equation

Fig. 1. A schematic representation of the structure of the governing equations and boundary conditions for salt-film problem.



SCHEMATIC DIAGRAM OF SYSTEM

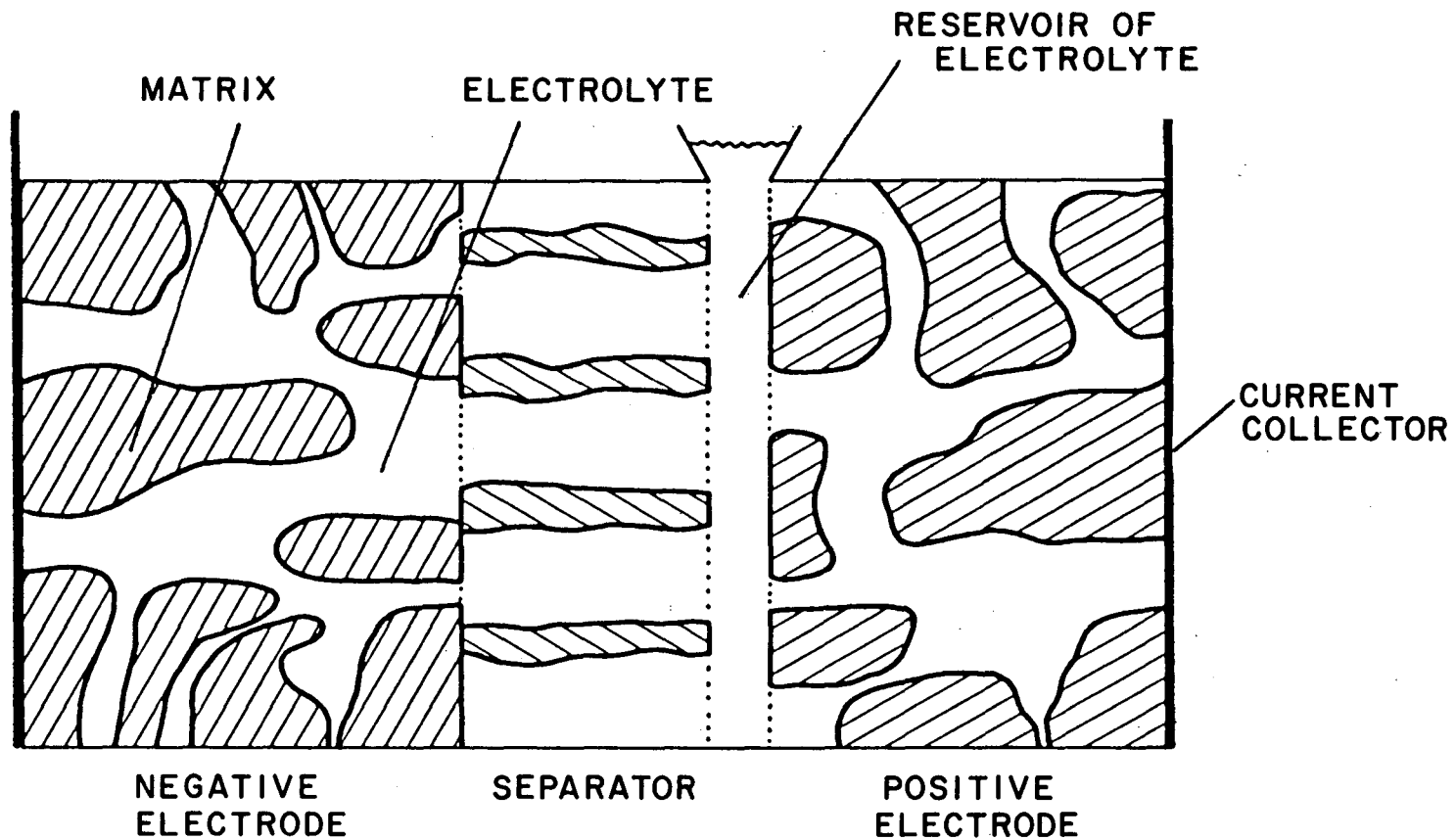
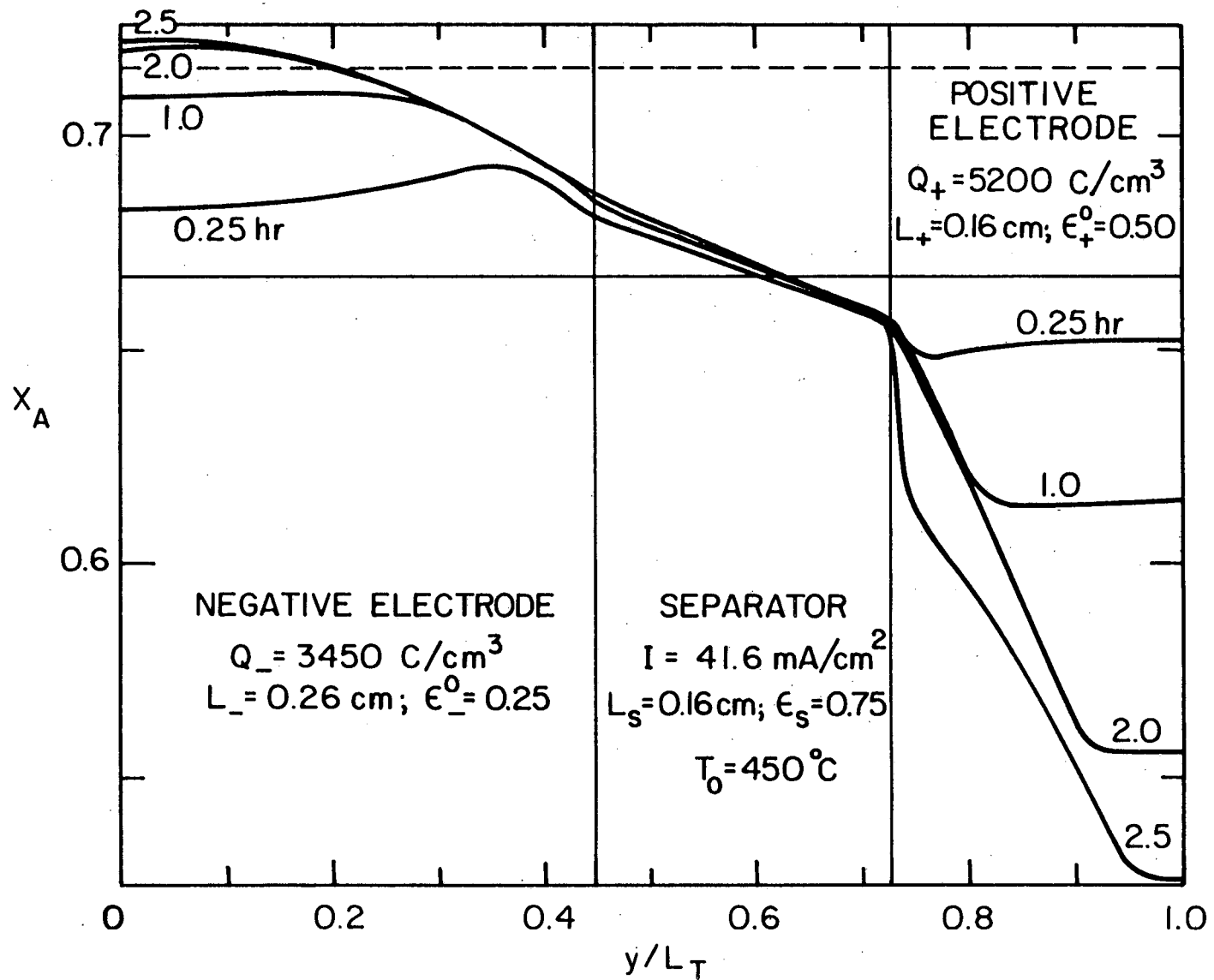


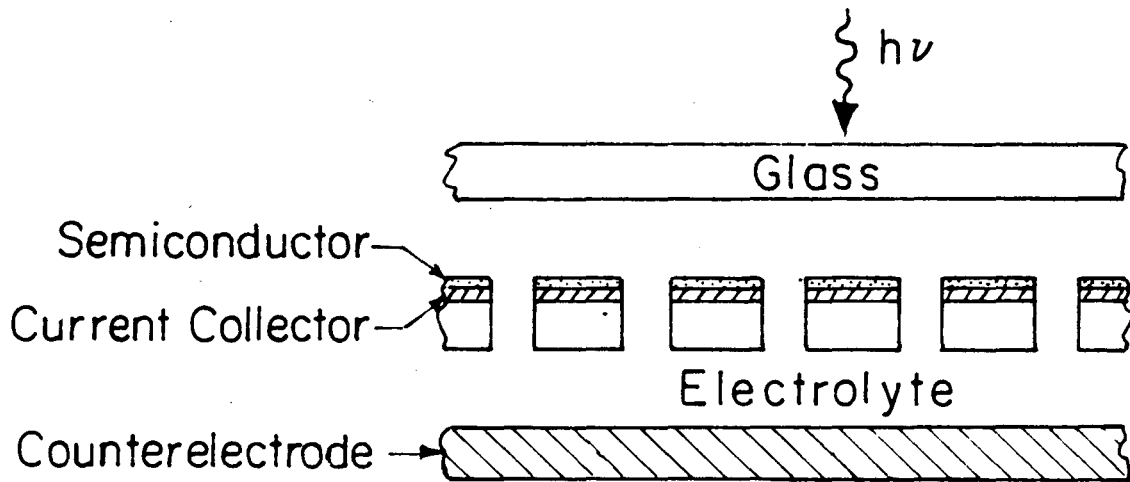
Fig. 2. Schematic diagram of LiAl/FeS cell.

XBL 7910-12435



XBL 7910-7169A

Fig. 3. Position dependence of mole fraction of LiCl at different discharge times. Dashed line represents saturation limit for LiCl at  $450^\circ\text{C}$ .



XBL 831-7974A

Fig. 4. Schematic diagram of the slotted-semiconductor photovoltaic cell.

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